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In re Patent Application of

KOMETANI et al

Atty. Ref.: 380-45; Confirmation No. 3708

Appl. No. 10/724,608

TC/A.U. 1711

Filed: December 2, 2003

Examiner: Sergeant

For: CATALYST FOR PRODUCTION OF A TWO COMPONENT POLYURETHANE
SEALANT

* * * * *

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

EVIDENTIARY DECLARATION UNDER 37 C.F.R. §1.132

I, Hiroyuki Kometani, am an inventor in the above-identified application, do hereby
declare:

1. That my residence and citizenship are of record in this application as stated in my
declaration as inventor made under 37 C.F.R. §1.63.

2. That I am employed by Tosoh Corporation of Tokyo, Japan, the assignee of this
application.

3. That I am familiar with the contents of the above-identified application and the
research effort underlying this application, and that I have read and am familiar with the Official
Action of December 13, 2005 and the Hagio et al, Laas et al, Nakamura et al and Hannah et al
references cited therein.

4. The above-identified application includes experiments and studies as given in Table 3
on page 22. I have undertaken a series of further experiments to show the beneficial results of

the inventive catalyst and methods of its use over a broad range of isocyanates and polyols as illustrated in the following table:

	Polyether polyol	Polyester polyol	Polymer polyol	Flame retardant polyol
MDI	Formulation B			
TDI	Formulation C			
MDI base prepolymer	Formulation A (Already disclosed in Table 3 on page 22)	Formulation E	Formulation F	Formulation G
TDI base prepolymer	Formulation D			

That I conducted various experiments based upon the above outline and the data contained in the following Tables was prepared by me. Polyurethane sealants were prepared using the catalysts prepared in Examples 1 to 6 of the subject application following the procedures of Examples 7 to 12 and reporting the results in a similar manner as these examples.

Table-4

	Example-7	Example-8	Example-9	Example-10	Example-11	Example-12
<u>Catalyst (pbw)</u>						
DBU-A	1.08	—	—	—	—	—
DBU-M	—	1.62	—	—	—	—
DBU-K	—	—	1.55	—	—	—
DBU-T	—	—	—	1.24	—	—
DBN-A	—	—	—	—	0.93	—
DBD-A	—	—	—	—	—	1.50
<u>Reactivity (sec)</u>						
Pot life ⁽¹⁾	826	760	847	771	812	805
Time V _i -2000 ⁽²⁾	846	808	946	956	912	952
Time V _i -4000 ⁽³⁾	853	816	957	977	936	966
Foaming property ⁽⁴⁾	○	○	○	○	○	○

1)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

2)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

3)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

4)No foaming :○ Foaming :×

Table-5

	Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex.4	Comp. Ex.5	Comp. Ex.6	Comp. Ex.7	Comp. Ex.8
<u>Catalyst (pbw)</u>								
DBU-A2	1.41	—	—	—	—	—	—	—
DBU-F	—	1.32	—	—	—	—	—	—
DBU-EH	—	—	1.58	—	—	—	—	—
DBU-S	—	—	—	7.76	—	—	—	—
DBD-FM	—	—	—	—	4.41	—	—	—
DBN-Ph	—	—	—	—	—	0.77	—	—
Thorcat535 ⁽¹⁾	—	—	—	—	—	—	0.5	—
Oct-Pb ⁽²⁾	—	—	—	—	—	—	—	0.002
<u>Reactivity (sec)</u>								
Pot life ⁽³⁾	694	672	312	1190	1355	576	688	550
Time Vi-2000 ⁽⁴⁾	862	691	386	---	---	751	808	720
Time Vi-4000 ⁽⁵⁾	917	697	435	---	---	802	837	815
<u>Foaming property⁽⁶⁾</u>	○	○	○	○	○	○	○	○

1)Mercury catalyst

2)Lead octylate (Pb:20wt%)

3)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

4)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

5)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

6)No foaming :○ Foaming :×

Table 4. Formulation-B

	pbw
Polyol ⁽¹⁾	24
Polyol ⁽²⁾	72
Zeolite 3A	4
Catalyst	Changed
MDI ⁽³⁾	Index=105

(1) Polyether polyol HV=376m gKOH/g

(2) Polyether polyol HV=56m gKOH/g

(3) Polymeric MDI, NCO Content=31.2%

Table-6

	Example-1	Example-1	Example-1	Example-16
Catalyst (pbw)				
DBU-A	1.08	—	—	—
DBU-M	—	1.62	—	—
DBU-K	—	—	1.55	—
DBU-T	—	—	—	1.24
Reactivity (sec)				
Pot life ⁽¹⁾	611	603	623	630
Time Vi-2000 ⁽²⁾	632	625	697	704
Time Vi-4000 ⁽³⁾	640	634	718	719
Foaming property ⁽⁴⁾	○	○	○	○

1) Time until the viscosity of the polyurethane sealant reaches 1000m Pa.s.

2) Time until the viscosity of the polyurethane sealant reaches 2000m Pa.s.

3) Time until the viscosity of the polyurethane sealant reaches 4000m Pa.s.

4) No foam ing : ○ Foam ing : ×

Table-7

	Com p. Ex.9	Com p. Ex.10	Com p. Ex.11	Com p. Ex.12	Com p. Ex.13
<u>Catalyst (pbw)</u>					
DBU-F	1.32	—	—	—	—
DBU-EH	—	1.58	—	—	—
DBU-S	—	—	7.76	—	—
Thorcat535 ⁽¹⁾	—	—	—	0.5	—
Oct-Pb ⁽²⁾	—	—	—	—	0.002
<u>Reactivity (sec)</u>					
Pot life ⁽³⁾	375	261	1120	610	310
Time Vi-2000 ⁽⁴⁾	420	298	---	751	487
Time Vi-4000 ⁽⁵⁾	435	372	---	799	522
<u>Foam ing property⁽⁶⁾</u>	○	○	○	○	○

1)Mercury catalyst

2)Lead octylate (Pb:20wt%)

3)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

4)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

5)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

6)No foam ing :○ Foam ing :×

Table 8. Formulation-C

	pbw
Polyol ⁽¹⁾	24
Polyol ⁽²⁾	72
Zeolite 3A	4
Catalyst	Changed
TDI ⁽³⁾	Index=105

(1) Polyether polyol OHV=376mgKOH/g

(2) Polyether polyol OHV=56mgKOH/g

(3) T-80;2,4-TDI/2,6-TDI=80/20

Table-9

	Example-15	Example-14	Example-13	Example-16
<u>Catalyst (pbw)</u>				
DBU-A	1.08	—	—	—
DBU-M	—	1.62	—	—
DBU-K	—	—	1.55	—
DBU-T	—	—	—	1.24
<u>Reactivity (sec)</u>				
Pot life ⁽¹⁾	602	588	611	618
Time Vi-2000 ⁽²⁾	628	624	702	705
Time Vi-4000 ⁽³⁾	642	640	723	728
Foaming property ⁽⁴⁾	○	○	○	○

1)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

2)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

3)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

4)No foaming : ○ Foaming : ×

Table-10

	Comp. Ex.9	Comp. Ex.10	Comp. Ex.11	Comp. Ex.12	Comp. Ex.13
<u>Catalyst (pbw)</u>					
DBU-F	1.32	—	—	—	—
DBU-EH	—	1.58	—	—	—
DBU-S	—	—	7.76	—	—
Thorcat535 ⁽¹⁾	—	—	—	0.5	—
Oct-Pb ⁽²⁾	—	—	—	—	0.002
<u>Reactivity (sec)</u>					
Pot life ⁽³⁾	364	247	1088	587	301
Time Vi-2000 ⁽⁴⁾	446	354	---	780	498
Time Vi-4000 ⁽⁵⁾	482	421	---	834	565
Foaming property ⁽⁶⁾	○	○	○	○	○

1)Mercury catalyst

2)Lead octylate (Pb:20wt%)

3)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

4)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

5)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

6)No foaming : ○ Foaming : ×

Table 11. Formulation-D

	pbw
Polyol ⁽¹⁾	24
Polyol ⁽²⁾	72
Zeolite 3A	4
Catalyst	Changed
Isocyanate prepolymer ⁽³⁾	Index=105

(1) Polyether polyol HV=376m gKOH/g

(2) Polyether polyol HV=56m gKOH/g

(3) MDI base prepolymer, NCO Content=21.0%

Table-12

	Example-17	Example-18	Example-19	Example-20
<u>Catalyst (pbw)</u>				
DBU-A	1.08	—	—	—
DBU-M	—	1.62	—	—
DBU-K	—	—	1.55	—
DBU-T	—	—	—	1.24
<u>Reactivity (sec)</u>				
Pot life ⁽¹⁾	834	771	855	797
Time Vi-2000 ⁽²⁾	857	824	964	974
Time Vi-4000 ⁽³⁾	869	835	978	998
Foaming property ⁽⁴⁾	○	○	○	○

1) Time until the viscosity of the polyurethane sealant reaches 1000m Pa.s.

2) Time until the viscosity of the polyurethane sealant reaches 2000m Pa.s.

3) Time until the viscosity of the polyurethane sealant reaches 4000m Pa.s.

4) No foaming : ○ Foaming : ×

Table-13

	Comp. Ex.14	Comp. Ex.15	Comp. Ex.16	Comp. Ex.17	Comp. Ex.18
<u>Catalyst (pbw)</u>					
DBU-F	1.32	—	—	—	—
DBU-EH	—	1.58	—	—	—
DBU-S	—	—	7.76	—	—
Thorcat535 ⁽¹⁾	—	—	—	0.5	—
Oct-Pb ⁽²⁾	—	—	—	—	0.002
<u>Reactivity (sec)</u>					
Pot life ⁽³⁾	684	334	1240	675	566
Time Vi-2000 ⁽⁴⁾	716	425	---	821	735
Time Vi-4000 ⁽⁵⁾	732	468	---	856	849
Foam ing property ⁽⁶⁾	○	○	○	○	○

1)Mercury catalyst

2)Lead octylate (Pb:20wt%)

3)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

4)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

5)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

6)No foam ing :○ Foam ing :×

Table 14. Formulation-E

	pbw
Polyol ⁽¹⁾	96
Zeolite 3A	4
Catalyst	Changed
Isocyanate prepolymer ⁽²⁾	Index=105

(1) Polyester polyol HV=450mgKOH/g

(2) MDI base prepolymer, NCO Content=26.0%

Table-15

	Example-21	Example-22	Example-23	Example-24
<u>Catalyst (pbw)</u>				
DBU-A	1.08	—	—	—
DBU-M	—	1.62	—	—
DBU-K	—	—	1.55	—
DBU-T	—	—	—	1.24
<u>Reactivity (sec)</u>				
Pot life ⁽¹⁾	822	757	846	778
Time Vi-2000 ⁽²⁾	841	801	931	964
Time Vi-4000 ⁽³⁾	852	816	946	984
Foam ing property ⁽⁴⁾	○	○	○	○

1)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

2)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

3)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

4)No foam ing :○ Foam ing :×

Table-16

	Comp. Ex.19	Comp. Ex.20	Comp. Ex.21	Comp. Ex.22	Comp. Ex.23
<u>Catalyst (pbw)</u>					
DBU-F	1.32	—	—	—	—
DBU-EH	—	1.58	—	—	—
DBU-S	—	—	7.76	—	—
Thorcat535 ⁽¹⁾	—	—	—	0.5	—
Oct-Pb ⁽²⁾	—	—	—	—	0.002
<u>Reactivity (sec)</u>					
Pot life ⁽³⁾	685	326	1210	684	524
Time Vi-2000 ⁽⁴⁾	709	398	---	824	708
Time Vi-4000 ⁽⁵⁾	722	457	---	867	829
Foaming property ⁽⁶⁾	○	○	○	○	○

1)Mercury catalyst

2)Lead octylate (Pb:20wt%)

3)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

4)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

5)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

6)No foaming :○ Foaming :×

Table 17. Formulation-F

	pbw
Polyol ⁽¹⁾	96
Zeolite 3A	4
Catalyst	Changed
Isocyanate prepolymer ⁽²⁾	Index=105

(1) Polymer polyol HV=22.0m gKOH/g

(2) MDI base prepolymer, NCO Content=26.0%

Table-18

	Exam p le-26	Exam p le-27	Exam p le-28	Exam p le-29
<u>Catalyst (pbw)</u>				
DBU-A	1.08	—	—	—
DBU-M	—	1.62	—	—
DBU-K	—	—	1.55	—
DBU-T	—	—	—	1.24
<u>Reactivity (sec)</u>				
Pot life ⁽¹⁾	838	768	858	819
T i m e V i-2000 ⁽²⁾	854	824	964	917
T i m e V i-4000 ⁽³⁾	868	832	976	949
Foam i n g p r o p e r t y ⁽⁴⁾	○	○	○	○

1)T i m e until the viscosity of the polyurethane sealant reaches 1000m Pa.s.

2)T i m e until the viscosity of the polyurethane sealant reaches 2000m Pa.s.

3)T i m e until the viscosity of the polyurethane sealant reaches 4000m Pa.s.

4)No foam i n g : ○ Foam i n g : ×

Table-19

	Com p. Ex.24	Com p. Ex.25	Com p. Ex.26	Com p. Ex.27	Com p. Ex.28
<u>Catalyst (pbw)</u>					
DBU-F	1.32	—	—	—	—
DBU-EH	—	1.58	—	—	—
DBU-S	—	—	7.76	—	—
Thorcat535 ⁽¹⁾	—	—	—	0.5	—
O c t-Pb ⁽²⁾	—	—	—	—	0.002
<u>Reactivity (sec)</u>					
Pot life ⁽³⁾	681	326	1284	704	560
T i m e V i-2000 ⁽⁴⁾	716	405	---	826	735
T i m e V i-4000 ⁽⁵⁾	728	437	---	897	823
Foam i n g p r o p e r t y ⁽⁶⁾	○	○	○	○	○

1)Mercury catalyst

2)Lead octylate (Pb:20w t%)

3)T i m e until the viscosity of the polyurethane sealant reaches 1000m Pa.s.

4)T i m e until the viscosity of the polyurethane sealant reaches 2000m Pa.s.

5)T i m e until the viscosity of the polyurethane sealant reaches 4000m Pa.s.

6)No foam i n g : ○ Foam i n g : ×

Table 20. Formulation-G

	pbw
Fram e Retardant Polyol ⁽¹⁾	96
Zeolite 3A	4
Catalyst	Changed
Isocyanate prepolymer ⁽²⁾	Index=105

(1) D i b r o m o n e o p n t y l G l y c o l / M o n o b r o m o n e o p n t y l T r i o l , O H V = 12.5m g K O H / g

(2) M D I b a s e p r e p o l y m e r , N C O C o n t e n t = 26.0%

Table-21

	Example-2	Example-3	Example-31	Example-32
<u>Catalyst (pbw)</u>				
DBU-A	1.08	—	—	—
DBU-M	—	1.62	—	—
DBU-K	—	—	1.55	—
DBU-T	—	—	—	1.24
<u>Reactivity (sec)</u>				
Pot life ⁽¹⁾	857	780	867	791
Time Vi-2000 ⁽²⁾	878	835	967	1024
Time Vi-4000 ⁽³⁾	889	849	978	1045
Foaming property ⁽⁴⁾	○	○	○	○

1)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

2)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

3)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

4)No foaming :○ Foaming :×

Table-22

	Comp. Ex.29	Comp. Ex.30	Comp. Ex.31	Comp. Ex.32	Comp. Ex.33
<u>Catalyst (pbw)</u>					
DBU-F	1.32	—	—	—	—
DBU-EH	—	1.58	—	—	—
DBU-S	—	—	7.76	—	—
Thorcat535 ⁽¹⁾	—	—	—	0.5	—
Oct-Pb ⁽²⁾	—	—	—	—	0.002
<u>Reactivity (sec)</u>					
Pot life ⁽³⁾	697	335	1310	698	573
Time Vi-2000 ⁽⁴⁾	719	421	---	826	746
Time Vi-4000 ⁽⁵⁾	735	457	---	868	846
Foaming property ⁽⁶⁾	○	○	○	○	○

1)Mercury catalyst

2)Lead octylate (Pb:20wt%)

3)Time until the viscosity of the polyurethane sealant reaches 1000mPa.s.

4)Time until the viscosity of the polyurethane sealant reaches 2000mPa.s.

5)Time until the viscosity of the polyurethane sealant reaches 4000mPa.s.

6)No foaming :○ Foaming :×

I declare further that all statements made herein of my/our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States

Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 6th June 2006

Hiroaki Kometani
Hiroaki Kometani

2.3.1.2 Prepolymer process [59]

Within the nomenclature of PU chemistry, prepolymers are understood as intermediates of the isocyanate polyaddition reaction. Numerous PU elastomers and almost all polyurethane-ureas are prepared via NCO prepolymer intermediates. This method allows for the complete reaction even of low reactivity polyether diols in absence of catalysts and for the intentional preparation of a segmented structure. The reaction between a diisocyanate and a diol is a second order reaction and depends on the molar ratio of the components. This makes it possible to prepare intermediates with the desired end groups and a defined average molecular weight in statistical distribution.

The possibility to tailor-make any desirable intermediate by the polyaddition reaction is a very important advantage of the diisocyanate polyaddition process compared with other polymerization processes. Specifically products with terminal NCO groups, so-called NCO prepolymers, are of substantial technical importance as intermediates in the synthesis of polyurethanes because they can be used with a multitude of active hydrogen containing compounds. They are generated by the reaction of di- or poly-hydroxyl compounds with a molar excess of di- or polyisocyanates and yield homogeneous mixtures which still contain a substantial percentage of the monomeric isocyanate. If diisocyanates with NCO groups of different reactivity are employed (2,4-diisocyanatotoluene, isophorondiiisocyanate), NCO prepolymers with narrow molecular weight distribution and small amounts of the starting diisocyanate are obtained. In all other cases requiring low monomer content, the excess diisocyanate has to be removed by distillation (preferably by thin layer evaporation) or extraction. If the NCO/OH ratio in the prepolymer preparation is greater than one, three, the resulting products are called semiprepolymer, because only a part of the available isocyanate is involved in the prepolymer formation. A lot of so-called "modified isocyanates" are this type of semi-prepolymers.

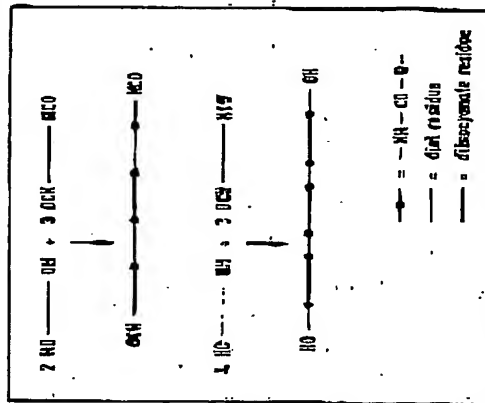


Fig. 2.1. NCO prepolymer and OH prepolymers

Polyurethane ureas [58]

The chain extension of NCO prepolymers with diamines is of substantial importance because the resulting polyurethane polymers are characterized by a high quality property level and reduced thermoplasticity. Generally aromatic diamines of low reactivity, which are sterically

hindered or which have reduced nucleophilicity due to electron withdrawing substituents, can be utilized. Amine chain extension has an advantage over glycol chain extension due to the fact that curing occurs fast and without further heat treatment which allows short production cycles. Usually, the NCO/NH₂-ratio is about one. The functionality of all reactants should be exactly two. Under these circumstances linear, uncrosslinked polyurethane polyureas of very high molecular weight, are obtained. The elastic character of these materials is attributed exclusively to the intermolecular forces between the hard segments.

A stoichiometric excess of NCO groups leads to reaction with already formed urea groups and subsequently to linear branching points leading to chemical crosslinking. As a result, the permanent stress retention is reduced, the polymers have reduced compression set and are insoluble in DMF. Also, chain extension of NCO-prepolymers by atmospheric humidity contained in the air leads to polyurethane polyureas and finally to polyurethane biurets. In the preparation of resins for coatings, this reaction is carried out also in absence of solvents.

2.3.2 Reactions in solution

Three discrete solvent systems have to be differentiated:

1. Completely reacted one-component systems, consisting of a high molecular weight linear polyurethane dissolved in a relatively polar solvent or solvent mixture.
2. Reactive one-component systems (prepolymers), which contain either free NCO groups or a heat active crosslinking system.
3. Reactive two-component systems.

2.3.2.1 Completely reacted one-component systems

These products dry physically. They contain a high molecular weight polyurethane, prepared according to the prepolymer process. The polyurethane is dissolved in a highly polar solvent (e.g., dimethylformamide) or in a solvent blend which solvates the soft segment, as well as the hard segment (e.g., methyl ethyl ketone/dimethylformamide). Diamines are used to carry out the final chain extension step. They are preferred not only because they react fast but also to obtain the final properties.

In case the polyaddition reaction is carried out in polar organic solvents (specifically in water-containing acetone or methyl ethyl ketone, in isopropyl alcohol/dimethylformamide), almost any diamine is suitable, even the very reactive aliphatic types, like ethylenediamine. As molecular weight increases, the solubility decreases and undissolvable pastes, gels or precipitates may be formed. Cycloaliphatic diisocyanates and diamines respectively increase the solubility. In the absence of ketones (e.g., in dimethyl formamide), aliphatic diamines react extraordinarily fast with the NCO groups of the prepolymers. Therefore, these diamines are reacted using the necessary precautions (i.e. cooling, vigorous mixing). Most often these reactions are carried out in a continuous manner, or the amines are used in the form of their CO₂ salts. This way it is possible to avoid side reactions (e.g., biuret formation) which lead to inhomogeneous polymer portions which are branched or crosslinked [60].

It is often desirable to impair the formation of hard segments in order to obtain better elastomer solubility. Here one adds a few mole percent of co-chain extenders (e.g., 1,2-propylene diamine, 1,3-diamide cyclohexane, piperazine, or even water) in addition to the chain extender (usually ethylenediamine) [60]. The highest molecular weight is obtained with equivalent amounts of NCO prepolymer and chain extender in dimethyl formamide. Excess or deficient amounts of chain extender lower the solution viscosity and allow the reaction of terminal NH₂ or NCO groups with e.g. di- or tri-isocyanates or monofunctional terminating agents, like butylamine [60].

In the case of cycloaliphatic diisocyanates with low reactivity, solutions of the NCO prepolymer in toluene can be reacted with a solution of diamine in isopropyl alcohol. Thereby, no reaction occurs between the NCO groups and the solvent (which would result in chain termination). One-component systems of this kind generally have a solvent content of 65–80%.

2.3.2.2 Reactive one-component systems

Relatively low molecular weight prepolymers with terminal NCO groups, which may be dissolved in small amounts of a solvent of low polarity (e.g., 75% in ethyl acetate), are cured by atmospheric humidity. The cure time is dependent on the relative humidity and the temperature. When applied in a thin layer the carbon dioxide, which is formed as a by-product, disappears without forming bubbles in the coating. NCO terminated one-component systems have limited storage stability (e.g., 6 to 12 months). The final products formed are crosslinked polyurethane films.

A second group of one-component systems consists of an OH-terminated prepolymer or an oligo-urethane (prepared from an NCO prepolymer reacted with a monofunctional chain extender) combined with a methylether-containing aminoplast resin. This mixture, dissolved in e.g., toluene/isopropyl alcohol at 40 to 50% solids content, is stable at room temperature but cures on the substrate after solvent evaporation at about 120 to 150 °C. Also, blocked NCO prepolymers, in combination with polyols or (blocked) amines are stable at room temperature and can be thermally cured upon the splitting off of the blocking agent.

2.3.2.3 Two-component systems

Two-component systems are commonly used in typical coatings, as well as leather and textile coatings applications. They consist predominantly of a polyhydroxy compound which may already be urethane-modified and an isocyanate adduct containing virtually no volatile diisocyanate. The most recent developments are directed towards making both components with a viscosity as low as possible in order to use the least amount of solvent ("high solids" systems). The solids content of the polyol component can be substantially increased by the use of a so-called "reactive diluent", e.g., a mono- or functional alcohol which can be built into the polymer (61).

2.3.3 Aqueous two-phase systems (62 to 65)

Prepolymers with terminal NCO groups can be mixed with water to yield reactive O/W emulsions; particularly when the molecular weight of the prepolymer does not exceed approx. 8,000. Prepolymers containing ionic centers (e.g., ammonium, sulfonium, sulfonate or carboxylate groups) or hydrophilic polyether segments are self-emulsifiable. This means that upon mixing with water they spontaneously form emulsions with particle sizes which decrease as hydrophilicity increases. The reactivity of NCO groups towards water increases in the same order. Hydrophobic NCO prepolymers necessitate the use of emulsifiers and high shear forces to disperse them in water. Emulsifiers which are chemically similar to the substrate to be dispersed are most efficient.

Highly viscous prepolymers must be diluted with organic solvents, which do not necessarily have to be miscible with water. The resulting aqueous emulsions can be further chain-extended/crosslinked by the addition of di- or polyamines. Specifically suited are highly reactive, only slightly water-soluble amines which have the ability to diffuse from the aqueous phase into the prepolymer droplets, thereby functioning as chain extenders/crosslinkers for the pendant NCO groups. In the absence of amines, chain extension will occur upon reaction with

Table 2.1 Characteristic features of polyurethane dispersions																
Dispersant vehicle	Acetone	Prepolymer	Melt-dispersion	Ketamine/ ketamine process	Solids self-dispersing process	Polyetheroxy compound (liquid)	Diisocyanate	Glycols	Dispersant	Solvent	Sugar free mix temperature of dispersion	Product before dispersion	Procedure after dispersion	End product	Solvent content of the final dispersion (g/g)	Post curing temperature
	force process					polyether (liquid) TDI	TDI only small amounts	variable	variable	40 to 70% acetone	-50 °C	polyurethane	active diisocyanate polyurethane polyurethane urea	polyurethane urea	2 to 8% toluene	700 to 3,000 100 °C
		force process				polyethers, active TDI, IPDI H ₁₂ MDI dimethylol prop- ionic acid	variable	variable	variable	often 10 to 30% N- methyl pyrrolidone	20 to 80 °C	NCO prepolymer	ionomer amine, extension polyurethane urea	polyurethane urea ionomer	often 5 to 15% N- methyl-pyrrolidone	50 to 150 °C 30 to 10,000
		process				variable		variable	variable	50 to 130 °C	50 to 80 °C	ion-bis-urea- prepolymers polycondensation	polyurethane polyurethane ketamine/ketamine possibly acetone distillation	polyurethane urea	possibly < 2% acetone	30 to 1,000
						variable		variable	variable	possibly 5 to 30% acetone	15 to 30 °C	NCO prepolymer + ketamine/ketamine	polyurethane urea	polyurethane	possibly < 2% acetone	30 to 500 > 130 °C

As a further step toward simplification of the cast technique, as well as improved industrial hygiene, the one component cast systems should be mentioned. Their technical perfection and material properties attainable at this time are not suitable for all requirements, which explain their limited scope. Generally they are ϵ -caprolactam blocked NCO prepolymers, primarily based on TDI-polyester, with aromatic diamines. Processing is extremely simple. It requires only heating the filled mold for several hours, during which the thermally labile caprolactam complex slowly dissociates. The NCO groups are released and react with the dissolved crosslinker to form thermally stable urea groups. The ϵ -caprolactam which is released remains in the casting as a contaminant and may be a cause of the reduced physical property values obtained with these elastomers. It is possible that the polar caprolactam is associated with the urea linkages, which hinders formation of the pseudo-crystalline hard segments, and acts as an internal lubricant between the polymer chains.

8.1.1.1 Raw materials

Diacyanates

As with all polyurethane application areas of technical importance, only a limited number of diisocyanate types are used for the production of cast elastomers. Most products are based on 4,4'-diisocyanatodiphenylmethane (MDI) or 2,4- or 2,6-toluene-diisocyanate. These basic components are used in pure, modified or prepolymer form.

In the hot cure systems, monomers diphenylmethane diisocyanate of predominantly 4,4'-isomer content finds widespread use. By increasing the content of the 2,4'-isomer, the melting point of the 4,4'-isomer (ca. 38°C) can be lowered. This leads to processing advantages, primarily in the cold cure systems. The differing reactivity of the two NCO groups in the isocyanate molecule and the altered steric structure in the polymer can be utilized to obtain special effects.

Modification of the MDI, for example, by partial carbodiimide formation or by reacting a portion of the NCO groups with polyol to form semi-prepolymers, serves to lower the melting point without changing the isomer content. Also, mixing with small amounts of polymeric MDI has the same effect.

Direct use of monomeric TDI for production of cast elastomers is relatively infrequent. In addition to industrial hygiene reasons, its use is conditional upon the differing reactivity of the NCO groups in the molecule. In nearly all cast systems based on TDI, the isocyanate comes in prepolymer form for use. A defined ratio of 2,4- and 2,6-isomer content may be favored, depending on the types of the other components.

The oldest high purity hot cure casting system is based on 1,4-naphthalenediisocyanate (NDI). The aliphatic diisocyanates, 1,6-diisocyanatohexane (HDI) and 1-isocyanato-3,3,3-trimethyl-5-isocyanatomethylcyclohexane (IPDI) and also the aromatic 4,4'-diisocyanato-3,3'-dimethylbiphenyl (TODI) only find application in very special cast systems. (Detailed descriptions of the isocyanates and their environmental concerns are found in Chapter 3; for a list of product names of the more important raw materials, see Chapter 15).

If storage precautions are observed, such as proper conditions of temperature and time (especially for MDI systems) and protection from moisture (necessary for all isocyanates and prepolymers), then most products of this type require no special preparation before use. Only higher viscosity types, such as NCO prepolymers, should be vacuum degassed at elevated temperature immediately prior to use in order to produce bubble free castings.

Polyols

Polyesters and polyethers are mainly used as the polyol component in the hot cure systems. Most polyesters are linear, hydroxyl terminated and between 1000 and 3000 molecular weight, generally around 2000. They are either comprised of one or two glycols with adipic acid, or

made by polymerizing ϵ -caprolactone. The polyester types, and in particular the glycol used in the polyadipates, influences the nature of the soft segment and therefore the physical properties (strength, low temperature behavior, elasticity, etc.) and the chemical resistance (mainly against hydrolytic attack) of the PU (see subsection 8.1.1.5).

Frequently, poly(tetrahydrofuran) is used as a polyol, which imparts especially good hydrolytic resistance. Only by use of special hydrolysis protection agents can the polyadipates attain this degree of hydrolytic stability.

Poly(oxyethylene-glycol) and poly(oxyethylene-oxypropylene-glycol) polyethers with molecular weights between 600 and 5000, and occasionally copolymer polyols, are used almost exclusively in the cold cure systems. They do not provide the high static and dynamic properties as the previously mentioned polyols. The same holds true for natural products which contain hydroxyl groups, such as castor oil (for detailed description of the polyols, see chapter 3; for a list of the most important trade names of the raw materials, see chapter 15).

All polyols, and polyesters in particular, absorb small amounts of moisture from the air during storage. Therefore, in order to avoid side reactions and produce bubble free castings, it is essential that they be dewatered before reacting with diisocyanate (see subsection 8.1.1.2). Generally the poly(oxypropylene glycols) only require a short degassing step in order to remove dissolved air.

Crosslinkers

As was mentioned earlier, short chain glycols or diamines are used as crosslinkers. Usually they are added separately, particularly in the hot cure system. The choice of a specific crosslinker depends on the reactants, processing technique and properties desired in the final products. TDI-based cast systems are usually crosslinked with aromatic diamines. Methylmethacrylate-chloroaniline (MCCA) has the widest application. The chlorine at the ortho position serves to reduce the reactivity of the amino group and permits good hand casting (see subsection 3.4). Developmental efforts for other aromatic diamine crosslinkers should consider the technical requirements of the processor (melting point of the diamine, manageable cast issues, etc.), the concerns of the end user (quality and price of the finished part), and certainly physiological considerations. The preferred approach has been aromatic diamines which contain ester groups, which do not accumulate in humans, since they can be biologically degraded (Chapter 14). Many materials of this type possess an excessively high melting point (> 170°C), or they are difficult to prepare. A few crosslinkers which give elastomers with outstanding properties have recently attained market importance. Of note is isobutyl 3,5-diamino-4-ethoxybenzoate (4). Also, 1,3-propane di-p-aminobenzoate ester esters or 4,4'-diaminodiphenylmethane-3,3'-dicarboxylic acids should be mentioned (5). It must be emphasized that processing and material properties are always dependent upon all components of the systems, and that an evaluation by comparison of the crosslinker alone is not valid. A similar biodegradation of aromatic diamines in humans, made possible by the ester groups, is attributed to the aminothiophenol derivatives. As the first product of this type, 1,2-ethylene-di-p-aminothiophenol has already been offered (6). Other diamines such as diethylthiophene-diamine, a mixture of isopropylthiophenediamine and *m*-phenylenediamine, both of which are liquid at room temperature, are not processable by hand casting because of their high reactivity. They must be processed by a metering and mixing machine (7) (see subsection 8.4).

Crosslinking through the use of a high melting, sterically hindered diamine, i.e. by mixing a powdered crosslinker into a moderately warmed prepolymer, is practical only in special cases. Many aromatic diamines form thermally labile addition complexes with various salts. This gives a special type of blocked crosslinker, which makes heterogeneous processing of the reactive diamine possible. The salt complex of 4,4'-diamino-diphenylmethane, (MDA), \cdot NaCl, dispersed in plasticizer is commercially available (8). Hot cure systems based

on MDI are nearly always crosslinked with glycol, primarily 1,4-butanediol. Occasionally, the hindered crosslinker hydroquinone-di- β -hydroxyethyl ether is used, which, in relatively low molar quantities, imparts a comparatively higher hardness and melting point to the hard segments. The resulting product exhibits a somewhat reduced thermoplastic character. Other glycols (ethylene glycol, 2,3-butanediol, 1,6-hexanediol, etc.) find only a secondary use. Triols, such as trimethylolpropane, occasionally are added in small amounts to the extender blend to achieve special effects.

The NDI cast system is nearly always extended with 1,4-butanediol and is crosslinked with other glycols only in special cases.

It is extremely important to maintain all glycol and amine crosslinkers free from moisture contamination in order to avoid bubble or foam formation during the isocyanate reaction. Absorption of atmospheric moisture during storage and handling is to be avoided.

8.1.1.2 Dewatering of the polyol

In light of the previous discussion, dewatering the polyol, especially the polyesters, is necessary. This can be accomplished in a batch process by heating ($> 400^\circ\text{C}$) in a reaction under vacuum ($< 60\text{ mm Hg}$). The length of this process depends on the amount of polyol, water content, reactor geometry, etc. In most cases, 2 to 3 hours of dewatering are sufficient. A continuous dewatering with simultaneous degassing is possible with a thin film evaporator. This gives a quick and precise temperature adjustment to the product, and is primarily suited to large volume throughputs.

Countercurrent hot air spray drying has not become practical since the oxygen content of the air frequently changes the reactivity of the polyol.

Water absorption by sodium aluminosilicates (Zeolites) is possible, based on the ability of the small water molecule to penetrate the cavity of the crystalline lattice. The larger organic molecules are excluded. These "molecular sieves" are used as a patio in castor oil or in other polyhydroxy compounds, since their drying ability is easily negated by exposure to moist air. The water absorption is reversible at elevated temperatures. Because of this and their mineral like consistency, they are seldom used in hot cast systems. They are limited to filled cold cure systems, where they have achieved widespread use.

8.1.1.3 Hot cure systems, production and processing

Prepolymer production by hand mixing

Isocyanate terminated MDI or NDI prepolymers frequently are made in a handmix by the processing industry themselves. In this way they can produce many grades of material from a few components simply by changing the formulation. In addition, this reduces the problems associated with prepolymer instability. For hand mixing of the prepolymer, the polyols are heated, dewatered and placed in a reaction vessel. The isocyanate is added in one shot, generally in a molar excess. Fig. 8.2 shows a sketch of a reaction apparatus. For practical purposes a reaction vessel is either an alloy steel pot, which can be cleaned by burning off the polymer, or a disposable polypropylene or tin can. The workability of the hard mix is not only limited by the size of the charge, but also by the reaction exotherm, which at higher temperatures, leads to side reactions (for example, carbodilimide or isocyanurate formation).

With liquid or low melting diisocyanates (MDI, TDI), the choice of starting temperature often serves as a control. Because of its high melting point (127°C), NDI cannot be added liquid to the polyol, so that an overheating of the prepolymer charge by the reaction exotherm is avoided. This process method of prepolymer formation frequently is used for production of high monomer containing prepolymers of limited storage stability.

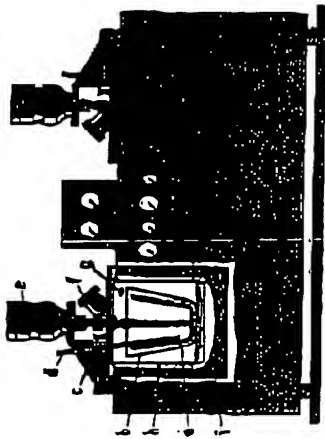


Fig. 8.2. Double reaction apparatus

a = anchor stirrer, b = casting pot, c = air petcock, d = thermometer, e = stirrer motor, f = oil port, g = vacuum line, h = heating medium, i = insulation

This mix ratio of the two components is determined by the properties (hardness) desired in the finished product. As already explained, excess of isocyanate, together with the crosslinker, forms the hard segment.

Large scale polymer production

As a rule, in a discontinuous or batch process, the isocyanate is charged first, and the polyol, adjusted to the proper temperature and viscosity, is slowly added (with cooling if necessary). Only this addition sequence of the components allows a good cleaning of the reaction between charges, since the production is always run on the NCO side.

Example 1:

18 pbw 2,4-toluene diisocyanate (TDI) is charged. With slow stirring, 82 pbw of a polyester of adipic acid and ethylene glycol (OH number 56) is added at a rate such that the reaction temperature does not exceed 60°C . Toward the end of the reaction, vacuum is applied for a short time, until an NCO value of 5.1% is attained. The reactivity of the prepolymer is reduced to such a degree that it can be added to a mixture of 1,4-butanediol and 1,6-hexanediol, etc.

Example 2:

58 pbw 4,4'-diisocyanatodiphenylmethane (MDI) and 5 pbw of a carbodilimide modified MDI (10% NCO) are charged at 40°C , and 37 pbw of a 56 OH number polyester produced from adipic acid and an equimolar mixture of 1,4-butanediol and 1,6-hexanediol is added at a rate to maintain the reaction temperature below 60°C . After 2 to 3 hours, an NCO value of 19% is attained. If necessary, the prepolymer can be stabilized as in the previous example.

Low monomer prepolymers

Low monomer prepolymers, primarily in the TDI systems, are becoming increasingly important. They exhibit a TDI monomer content of less than 0.7% and a corresponding decrease in vapor pressure. The realization of a pure 2:1 adduct did not succeed by reaction of 2 moles of diisocyanate with one mole of polyol, since by this method, it is not possible to prevent formation of multiple adducts (3:2, 4:3, etc.). In practice, a considerable excess of diisocyanate is charged, which, after reaction with the polyol, is removed by a thin film evaporation.

The foams were produced by mixing the diisocyanate with the polyester until the resulting exothermic reaction (formation of polyurethane) set off the gas evolution. At first polyesters of relatively high acid number (approximately 30 or more) were used in the manufacture of Moltopren. Later the tendency was to employ polyesters of low acid number and to control the foaming reaction by the addition of a measured amount of water instead of adjusting the acid number of the polyester (21).

Moltopren was used in filling aircraft parts, to improve the buoyancy of boats and ships, and for insulation.

The rigid foam applications in the German aircraft industry led the U. S. Air Force to place research contracts with Goodyear Aircraft Corp. as well as with other organizations. Work begun at Goodyear Aircraft Corp. in 1946 led to the development of low density foam core materials, which could be used for the construction of radomes. The materials used in the manufacture of the core consisted of an alkyl resin, made from glycerol, phthalic anhydride, and adipic acid, and tolylene diisocyanate (31). Lockheed Aircraft Corp., in 1947-1948, independently developed a technique for foamed-in-place rigid polyurethane foam (Lockfoam) and was granted a series of patents (43).

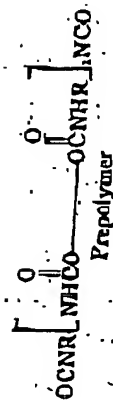
The commercial success of polyurethanes in postwar Germany, notable in the field of foams, brought about a considerable spur-of-activity on the part of American industry. In 1950, Du Pont and Monsanto started semicommercial production of diisocyanates, primarily aromatic ones. Du Pont, in 1953, announced a polyurethane foam and also provided information on its method of preparation via the prepolymer route. Bayer began to introduce its know-how into the United States slowly in 1953, and then with Monsanto formed Mobay in 1954. Through this means a considerable amount of German technology on polyurethanes was disseminated in the U. S. and German foam machines were imported which helped to speed up the commercial production of flexible foam. Du Pont, Mobay, and, to a lesser extent, Lockheed Aircraft Corp., extended licenses to foam manufacturers and provided technical assistance.

The urethane foam industry developed along lines indicated previously, first with diisocyanate-polyester combinations, more recently with diisocyanate-polyether combinations being used in the largest

volume. The polyester systems employed a "one-shot" technique in which polyester, diisocyanate, water, catalysts, and foam stabilizers were all mixed in one step, and permitted to foam. The first commercial use of polyethers employed a "prepolymer" process, wherein the polyether and diisocyanate were first reacted to form a "prepolymer" that was subsequently mixed with catalyst, water, and stabilizers to produce foam. By the end of 1958, a "one-shot" process for polyether-urethane foams, but with different catalysts and stabilizers than are used for polyester foams, was developed. This newer technology, and especially the very low foam densities available from it, marked a further economic improvement. Both foam producers and raw material suppliers contributed heavily to these developments.

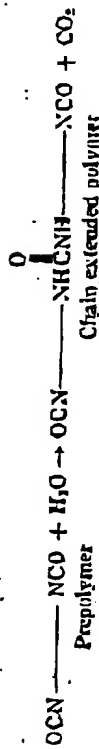
Synthetic elastomers comprise a fourth major application of polyurethanes. Whereas Schlack (42) and Christ and Hanford (9) in the United States noticed the formation of elastic urethane products, they did not pursue the subject further. To Pinten (33) goes the credit of preparing the first highly elastic isocyanate rubbers ("T rubbers"). These elastomers were prepared from diisocyanates and a polyester obtained by condensing a glycol, 4% of which was replaced with a trifunctional alcohol, with adipic acid. The "T rubbers" of Pinten had high tensile strength and abrasion resistance but poor tear resistance, and exhibited changes in elongation and hardening on exposure to low temperatures.

Bayer and co-workers (5) reported extensive investigations on polyurethane elastomers, leading to the development of Vulcolan rubbers. The first step consisted in the reaction of linear hydroxyl-terminated polyesters, made from glycols and dibasic acids, with a diisocyanate to form a prepolymer:

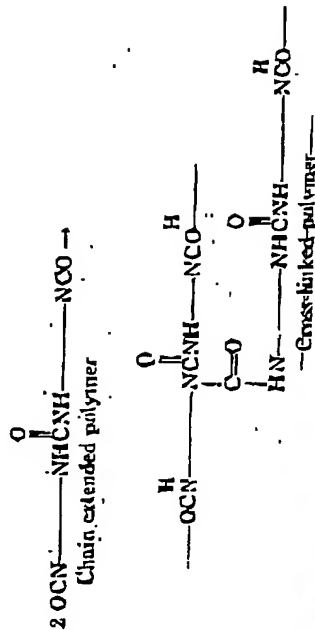


The glycols used in the manufacture of the linear polyesters were varied, although ethylene and propylene glycols or mixtures of the two were preferred; adipic acid was the standard acid. Aromatic diisocyanates, particularly 1,5-naphthalene diisocyanate, were found to be especially suited for urethane rubbers.

The prepolymer was then chain extended with a controlled amount of water, forming urea groups and leaving about 2-5% of unreacted isocyanate groups:



The cross linking of the chain extended polymer then took place at elevated temperatures (125-150°C.) through the reaction of the excess isocyanate groups with the active hydrogen on either the urea or the urethane groups in the polymer chain. Since the urea group reacts much faster than the urethane group, this is the favored curing reaction:



Several methods were used in the preparation of Vulcanin, and it was soon recognized that other chain extenders such as glycols, diamines, or amino alcohols, could be used (29).

Polyurethane elastomers were also investigated in England and the United States. The English Vulcaprene-A was developed through the work of Imperial Chemical Industries (16) whereby the polyester component was replaced with a polyesteramide. In the United States, Goodyear Tire and Rubber Co. brought out a polyurethane rubber, Chemigum SL (12). The latter was made by using a deficit of diisocyanate in the reaction with polyesters, thereby forming an uncured gum stock, which was storable and which could be cured with additional amounts of diisocyanate. Du Pont developed their own line of polyurethane rubbers (Adiprene); which were based on poly(oxytetramethylene) glycols rather than polyesters (19,37).

Fabrication methods for urethane elastomers underwent a significant development. While most of the early urethane rubbers were pre-

pared on conventional rubber equipment, a liquid-rubber casting technique described by Müller *et al.* (29) permitted the manufacture of many rubber goods at considerable savings in fabrication costs.

In addition to these major areas of applications, isocyanates have been used for a variety of purposes, including the waterproofing of textiles; tanning leather, modifying many polymers, and as chemical intermediates, particularly in the pharmaceutical field.

In recent years several companies have joined the ranks of the isocyanate suppliers. Carwin Chemical Company was one of the first, offering a variety of specialty isocyanates for elastomers, adhesives, coatings, specialty foams, and other uses. Recently Nöpcó Chemical Company announced plans for the large scale manufacture of tolylene diisocyanate in the near future. Ott Chemical Company is a recent supplier of aliphatic monoisocyanates.

The development of the urethane industry has been accompanied by the publication of many excellent reviews of the preparation of isocyanates (1,28,39,41), their reactions (1,28,38,39), and commercial applications (4,7,11,13,20,21,28,40).

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